Report for 2001DC4061B: Speciation of Tributyltin and Triphenyltin Compounds in Clays from Sediments Using Mossbauer Spectroscopy

There are no reported publications resulting from this project.

Report Follows:

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Speciation of Tributyltin and Triphenyltin Compounds in Clays from Sediments Using Mõssbauer Spectroscopy

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Introduction

Previously, we had examined the speciation of tributyltin (TBT) and triphenyltin (TPT) compounds directly in sediments from the Anacostia River (5), Baltimore Harbor (1), Chesapeake Bay (2- 4), and Potomac River (5). Tin Mössbauer spectroscopy was used to determine the nature of the tin compounds in the sediments. It was found that the speciation of triorganotin compounds varies with the nature of the sediment. It is important to determine which component or components of the sediment are involved in the speciation of the tin compound. The Anacostia and Potomac Rivers are in the Washington Quadrangle of which one-fourth is in the Piedmont Plateau and the remainder in the Coastal plain (6). Clays are one of the important components of these formations. For example, it has been reported that kaolin is one of the clays that have been found (6, p. 27).

X-Ray Diffraction of Sediments

X-ray diffraction of dried sediments from the Anacostia (AR-1) and Potomac Rivers (PR10) was measured using the LabX, XRD-6000 (Shimadzu, Co.). Some of the major lines in the x-ray patterns are shown in Table 1 with the assignments of the lines. Both samples contained as a major constituent, a-quartz, and clays plus other constituents such as goethite. The clays included kaolinite, illite, smectite, and chlorite.

Mössbauer Spectroscopy

The following procedure was used in all experiments: Mixtures of 5 g of the clay sample (kaolinite, Sullivan's Grove, Md., Potomac River) or sand and 5 mL of solution containing the organotin compound amounting to 3.3 % were shaken mechanically in closed test tubes for two weeks at room temperature. After remaining at room temperature for two additional weeks, the sample was removed by gravity filtration and kept frozen until the Mössbauer spectrum is measured. The Mössbauer spectra were measured at 80K on a Mössbauer spectrometer model MS-900 (Ranger Scientific Co.) in the acceleration mode with moving source geometry.

The results are presented in Tables 2 and 3 compared with results of spectra found with speciation studies in sediments from the Anacostia (AR) and Potomac (PR) Rivers (5). The initial results show that the TPTCl has the same Mössbauer parameters in kaolinite as in the sediments and as a neat sample. This suggests that it was unchanged in these media. The same is found for TPTOH in kaolinite and sand indicating that the compound was probably converted to the chloride. The results for TBTO are not reproducible and require additional samples to be mixed with both the clay and sand. Both the quadrupole splittings and the isomer shifts are different in the two sets of samples. In one sample of TBTCl and kaolinite, the Mössbauer parameters of the tin compound was the same as the parameters of the neat sample of the tin compound.

Future Studies

It is planned to continue the studies on the speciation between the clay and sand and the triorganotin compounds TPTCl, TPTOH, TBTO, TBTCl and expand the speciation with the acetates of TPT and TBT. Other clays that can be purchased include illite, montmorillonite and smectite (nontronite). We are also starting the study of the infrared spectra of the tin compounds with the components to determine the nature of the interaction.

Literature Cited

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Table 1.Selected Lines in the X-Ray Patterns of Sediments from the Anacostia (Left-AR 1) and Potomac (Right-PR 10) Rivers

Number	2?	I/I_{max}	Assignment	Number	2?	I/I_{max}	Assignment
1	8.88	9	Illite	1	5.80	3	Smectite
3	17.79	6	Goethite	2	8.96	22	Illite
4	20.85	16	a-Quartz	5	17.79	9	Goethite
6	26.63	100	a-Quartz	7	20.85	20	a-Quartz
9	45.58	8	Kaolinite	10	26.63	100	a-Quartz
				14	40.32	4	Chlorite

Table 2. Mössbauer Spectra of Triphenyltin (TPT) Compounds in Sediments and Components

Compound	Medium	QS Aerobic	IS Aerobic	QS Anaerobic	IS Anaerobic	Ref.
TPTCl	Neat	2.62(7)	1.35(2)			2
	AR 1	2.81(5)	1.20(1)	2.83(3)	1.13(1)	5
	AR 2	2.80(7)	1.30(2)	2.82(3)	1.23(1)	5
	AR 4	2.60(3)	1.28(7)	2.83(3)	1.22(1)	5
	AR 6	2.74(5)	1.17(1)	2.79(3)	1.21(1)	5
	PR 4	2.75(3)	1.17(1)	2.74(2)	1.17(1)	5
	PR 7	2.85(7)	1.20(2)	2.79(3)	1.22(1)	5
	PR 9	2.83(3)	1.19(1)	2.85(2)	1.20(1)	5
	PR 10	2.88(3)	1.21(1)	2.84(2)	1.20(1)	5
	Kaolinite	2.70(3)	1.34(1)			a.
	Kaolinite	2.61(5)	1.26(1)			a
	Sand	2.56(5)	1.34(1)			a
TPTOH	Neat	2.95(7)	1.23(7)			2
	AR 1	2.76(3)	1.18(1)	2.76(3)	1.16(1)	5
	AR 2	2.91(4)	1.21(1)	2.74(2)	1.18(1)	5
	AR 4	2.75(3)	1.17(1)	2.77(3)	1.19(1)	5
	AR 6	2.74(5)	1.18(1)	2.76(2)	1.21(1)	5
	PR 4	2.79(3)	1.18(1)	2.78(2)	1.18(1)	5
	PR 7	2.76(5)	1.18(1)	2.73(3)	1.20(1)	5
	PR 9	2.83(4)	1.23(1)	2.72(3)	1.14(1)	5
	PR 10	2.75(3)	1.18(1)	2.79(4)	1.22(1)	5
	Kaolinite	2.73(2)	1.14(1)			a
	Sand	2.78(5)	1.20(1)			a

a- This work.

QS = Quadrupole Splitting; IS = Isomer Shift

Table 3. Mössbauer Spectra of Tributyltin (TBT) Compounds in Sediments and Components

Compound	Medium	QS Aerobic	IS Aerobic	QS Anaerobic	IS Anaerobic	Ref.
TBTO	Neat	1.55(5)	1.11(1)			1
	Water	3.06(8)	1.41(1)			1
	Seawater	3.06(6)	1.37(2)			1
	AR 1	3.27(4)	1.39(1)	3.21(5)	1.39(1)	5
	AR 2	3.30(6)	1.47(1)	3.32(5)	1.47(1)	5
	AR 4	3.16(6)	1.38(2)	3.19(4)	1.44(1)	5
	AR 6	3.25(6)	1.46(1)	3.23(5)	1.41(1)	5
	PR 4	3.41(7)	1.34(2)	3.13(5)	1.43(2)	5
	PR 7	3.21(6)	1.44(3)	3.17(4)	1.41(1)	5
	PR 9	3.10(8)	1.47(2)	3.07(3)	1.36(1)	5
	PR 10	2.97(5)	1.44(1)	3.10(3)	1.43(1)	5
	Kaolinite	3.84(3)	1.49(1)			a
	Kaolinite	2.16(3)	1.03(1)			a
	Sand	2.96(5)	1.42(1)			a
	Sand	2.11(3)	1.05(1)			a
TBTCl	Neat	3.43(4)	1.56(1)			1
	Water	3.40(4)	1.55(1)			1
	Seawater	2.81(7)	1.36(7)			1
	AR 1	3.42(4)	1.53(1)	3.25(2)	1.43(6)	5
	AR 2	3.23(8)	1.39(2)	3.32(2)	1.45(1)	5
	AR 4	3.30(5)	1.39(1)	3.23(3)	1.39(1)	5
	AR 6	2.91(5)	1.25(1)	3.32(4)	1.43(1)	5
	PR 4	3.19(5)	1.43(1)	3.06(7)	1.37(1)	5
	PR 7	3.24(8)	1.33(2)	3.38(7)	1.45(2)	5
	PR 9	3.29(4)	1.41(1)	3.40(7)	1.51(2)	5
	PR 10	3.76(6)	1.62(2)	3.35(3)	1.44(1)	5
	Kaolinite	3.43(3)	1.47(7)			a

a-This work.

QS = Quadrupole Splitting; IS = Isomer Shift